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Intermediates in the Synthesis of (+)-Grandisol. II†

J. Zukerman-Schpector[a]* and Hugo J. Monteiro[b]

[a]*Laboratório de Cristalografia, Estereodinâmica e Modelagem Molecular, Depto. Química, Universidade Federal de São Carlos, Caixa Postal 676, 13565-905 – São Carlos, SP, Brazil, and* [b]*Depto. Química, Universidade de Brasília, 70910-900 – Brasília, DF, Brazil. E-mail: julio@power.ufscar.br*

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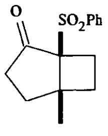
Abstract

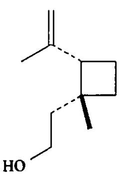
In the compound (1*S*,5*S*)-5-methyl-1-(phenylsulfonyl)bicyclo[3.2.0]heptan-2-one, $C_{14}H_{16}O_3S$, the cyclopentanone ring is in a twist conformation and the cyclobutane ring is puckered. The phenylsulfonyl and methyl groups are *cis* with respect to each other.

Comment

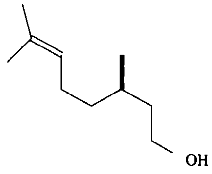
The terpene (+)-*cis*-2-isopropenyl-1-methylcyclobutaneethanol, (2), *i.e.* (+)-grandisol (Tumlinson *et al.*, 1971), is the principal component in the aggregation pheromone produced by the male cotton boll weevil, *Anthonomus grandis* Boheman (Franke *et al.*, 1989), which is a serious pest in Brazilian cotton fields. The potential use of this terpene in traps for monitoring crop infestation in integrated pest management makes it a target for synthetic organic chemists, especially the more active (+)-enantiomer (Dickens & Mori, 1989). As the success of a synthetic route aimed at the synthesis of (+)-grandisol, starting with the easily available (+)-citronellol, (3), depends on the generation of intermediates with the correct functionality and stereochemistry, their unambiguous stereostructure determination is required. We report here the crystal structure determination of another intermediate, (1).



(1)



(2)



(3)

The S atom is tetrahedrally bonded to two C and two O atoms, with tetrahedral angles ranging from 106.5 (2) to 108.9 (2)°, except for the O—S—O angle which is 118.6 (3)°. The phenylsulfonyl and methyl groups are *cis* with respect to each other, the rings being *cis*-fused. The Cremer & Pople (1975) puckering parameters show that the five-membered ring is in a twist conformation; $q_2 = 0.221\,(6)$ Å and $\Phi_2 = 119\,(1)°$. The four-membered ring is puckered, with a dihedral angle between C1, C7, C5 and C5, C6, C7 of 19 (1)°, making a dihedral angle of 71.2 (2)° with the least-squares plane through the five-membered ring. The phenyl ring makes dihedral angles of 24.5 (4) and 48.5 (3)° with the five- and four-membered rings, respectively. The O atom of the cyclopentanone ring was found to be disordered. A difference map indicated, however, that the disorder could be satisfactorily described by a simple model postulating two different orientations.

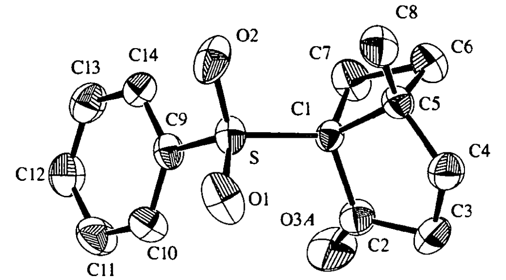


Fig. 1. The molecular structure of (1) showing 40% probability displacement ellipsoids, only the major component of the disordered O atom is shown. H atoms have been omited for clarity.

Experimental

The synthesis of the title compound is described in Monteiro & Zukerman-Schpector (1996). Crystals were obtained from CH_2Cl_2–hexane by slow evaporation at 269 K.

Crystal data

$C_{14}H_{16}O_3S$
$M_r = 264.33$
Orthorhombic
$P2_12_12_1$
$a = 7.4828\,(8)$ Å
$b = 12.126\,(1)$ Å
$c = 14.179\,(2)$ Å
$V = 1286.6\,(3)$ Å^3
$Z = 4$
$D_x = 1.365$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.87–17.30°$
$\mu = 0.249$ mm^{-1}
$T = 293$ K
Prismatic
0.40 × 0.15 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1795 measured reflections
1795 independent reflections
1085 reflections with $F^2 > 2\sigma(F^2)$

$\theta_{max} = 28.0°$
$h = 0 \rightarrow 9$
$k = -16 \rightarrow 0$
$l = 0 \rightarrow 18$
2 standard reflections
frequency: 30 min
intensity decay: 0.9%

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† Part I: Zukerman-Schpector & Monteiro (1996).

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.0857$
$S = 1.078$
1795 reflections
174 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2$
$+ 0.566P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.279$ e Å^{-3}
$\Delta\rho_{\min} = -0.234$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.0 (3)

Table 1. *Selected geometric parameters (Å, °)*

S—O2	1.426 (4)	C1—C5	1.572 (5)
S—O1	1.444 (3)	C5—C8	1.506 (6)
S—C9	1.769 (4)	C5—C6	1.551 (6)
S—C1	1.780 (4)	C6—C7	1.530 (6)
C1—C7	1.532 (5)		
O2—S—O1	118.6 (3)	C7—C1—S	118.0 (3)
O2—S—C9	106.5 (2)	C5—C1—S	119.9 (3)
O1—S—C9	108.9 (2)	C8—C5—C4	111.8 (4)
O2—S—C1	108.1 (2)	C8—C5—C6	113.7 (4)
O1—S—C1	107.1 (2)	C4—C5—C6	115.7 (4)
C9—S—C1	107.2 (2)	C8—C5—C1	120.8 (3)
C2—C1—C7	112.3 (3)	C4—C5—C1	105.9 (3)
C2—C1—C5	104.4 (3)	C6—C5—C1	86.8 (3)
C7—C1—C5	90.0 (3)	C7—C6—C5	90.9 (3)
C2—C1—S	110.4 (3)	C6—C7—C1	89.0 (3)

H atoms were refined using a riding model and with $U(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$ for methyl and $1.2U_{\mathrm{eq}}(\mathrm{C})$ for other groups.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1177). Services for accessing these data are described at the back of the journal.

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N,*N*′-Bis(1-methylimidazol-2-ylmethylidene)-1,3-diaminopropan-2-ol, HBIMPNOL

Ivo Vencato, Ademir Neves, Marciela Scarpellini and Valdir R. Correia

Departamento Química - UFSC, 88040-900 - Florianópolis, SC, Brazil. E-mail: vencato@qmc.ufsc.br

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Abstract

The crystal structure of the title compound, $C_{13}H_{18}N_6O$, reveals that for such a species to act as a tetradentate ligand, significant rearrangement is required, as evidenced by the dihedral angle [67.5 (1)°] between the two imidazole rings which results in a large separation of 7.256 (4) Å between the N donor atoms of these rings.

Comment

In recent years, it has been recognized that pentadentate Schiff base ligands derived from 1,3-diaminopropan-2-ol containing adequate pendant donor groups such as phenolate, pyridine, pyrrole or imidazole play an important role in the synthesis of model complexes for copper-containing metalloproteins (Butcher *et al.*, 1986*a*,*b*; Borer & Sinn, 1988; Mazurek *et al.*, 1985; Nishida & Kida, 1986). Specifically, the title ligand, HBIMPNOL, has displayed the ability to function as both a tetradentate and a dinucleating ligand (Borer & Sinn, 1988; Doman, Richardson, Arar & Buchanan, 1989). However, no X-ray structures of uncoordinated pentadentate ligands of this type have been reported previously. Moreover, a Cambridge Structural Database (1996) search shows that the X-ray crystal structure of a mononuclear Cu$^{\mathrm{II}}$ complex with HBIMPNOL is the only structure in the literature which contains the title ligand (Doman *et al.*, 1989). We have, therefore, determined the crystal structure of HBIMPNOL so that subsequent changes upon coordination may be investigated.

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